Studies of Phosphazenes. Part 14.[1] The Tautomerism of Oxocyclotriphosphazadienes

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The tautomeric behaviour of 'monohydroxycyclotriphosphazatrienes' has been investigated by ^{31}P n.m.r. spectroscopy. These derivatives exist as oxocyclotriphosphazadiene tautomers in which the hydrogen atom is attached to a ring nitrogen atom α to the phosphoryl group. Three types of prototropic behaviour are observed: (*a*) no exchange is detected and only one tautomer is present [*e.g.* $N_3HP_3(NHBu^t)_2R_3O$ (R = OMe or OEt)]; (*b*) exchange takes place between two equivalent sites and only one tautomer is observed [*e.g.* $N_3HP_3R_5O$ (R = OMe or OPh); $N_3HP_3Ph_4RO$ (R = OMe or OEt)]; and (*c*) exchange occurs between two non-equivalent sites and two tautomers are present [*e.g.* $N_3HP_3Ph_2R_3O$ (R = OMe, OEt, or OPr^n)]. It is shown that basicity calculations using substituent constants have predictive value since they are in good agreement with the spectroscopic observations.

CYCLOPHOSPHAZENE derivatives containing one or more hydroxy-substituents have been known since the nineteenth century [2-4] although many are poorly characterised.[3] 'Hydroxy' derivatives containing trifluoroethoxy- or aryloxy-groups have been reported in extensive studies of hydrolysis reactions by Allcock and Walsh.[5] Derivatives of the types $N_3P_3Ph_2R_3(OH)$ and $N_3P_3Ph_4R(OH)$ (R = alkoxy) were obtained by Fitzsimmons *et al.*[6] from alcoholysis reactions of the respective chloro(phenyl) precursors. It was suggested that these compounds exist in the oxocyclophosphazadiene form on the basis of their i.r. spectra. A similar conclusion was reached by Vîlceanu and Schulz [7] from an i.r. and ^1H n.m.r. study of the methoxy-derivative, $N_3P_3(OMe)_5(OH)$. Recently, *X*-ray crystallography has confirmed the oxocyclophosphazadiene structure for the derivatives, $N_3P_3Cl_2(NEt_2)_3(OH)$ [8] and $N_3P_3Ph_2(OMe)_3(OH)$.[9]

Four tautomeric structures are possible for a monohydroxycyclotriphosphazatriene, $N_3P_3R_3R'_2(OH)$ (Figure 1). In this paper, we show how dynamic ^{31}P n.m.r. spectroscopy can be used to determine the preferred tautomers in solution for compounds of this type. We also evaluate the utility of pK_a' calculations in predicting the most likely tautomeric form of hydroxycyclophosphazenes containing different substituents.

EXPERIMENTAL

Preparations.—(*a*) *gem*-$N_3HP_3(NHBu^t)_2(OMe)_3O$ (1).—The geminal bis(t-butylamino)-derivative, $N_3P_3Cl_4(NHBu^t)_2$ (5.0 g, 0.012 mol), was allowed to react with sodium methoxide as described previously.[1] After extraction of the methoxy-derivative,[1] $N_3P_3(NHBu^t)_2(OMe)_4$, with light petroleum † the insoluble residue was dissolved in diethyl ether (200 cm^3) and sodium chloride was filtered off. The filtrate was washed with dilute hydrochloric acid (100 cm^3), sodium hydrogencarbonate solution (100 cm^3), and water (3 × 75 cm^3), dried (Na_2SO_4), and the solvent distilled off. The resultant oil solidified on addition of light petroleum. A further quantity of the same solid (i.r. evidence) was obtained from the neutralised water washings by extraction with chloroform. Recrystallisation of the product from dichloromethane–light petroleum (1 : 5) gave 2,2,4-*trimethoxy*-4-*oxo*-6,6-*bis*(*t-butylamino*)*cyclotriphosphazadiene* (1), m.p. 189—192 °C (2.8 g, 60%) (Found: C, 33.4; H, 8.0; N, 17.7. $C_{11}H_{30}N_5O_4P_3$ requires C, 33.9; H, 7.7; N, 18.0%). Molecular weight in benzene by osmometry = 701 (calc. 778). ^1H N.m.r. ($CDCl_3$): δ(NH) 7.5_0 (ring), 3.4; δ(OMe) 3.57(1), 3.68(2), $^3J^*$(P–H) 12.4, 12.2 Hz; δ(CMe_3) 1.28.

(*b*) *gem*-$N_3HP_3(NHBu^t)_2(OEt)_3O$ (2). The ethoxy-compound (2) was prepared from $N_3P_3Cl_4(NHBu^t)_2$ (0.012 mol) and sodium ethoxide by the procedure given in (*a*). Extraction of the combined water washings with chloroform gave 2,2,4-*triethoxy*-4-*oxo*-6,6-*bis*(*t-butylamino*)*cyclotriphosphazadiene* (2), m.p. 194—196 °C (1.49 g, 35%) (Found: C, 38.8; H, 8.4; N, 15.9. $C_{14}H_{36}N_5O_4P_3$ requires C, 39.0; H, 8.3; N, 16.2%). ^1H N.m.r. ($CDCl_3$): δ(NH) 7.3_5 (ring), 3.1; δ(OCH_2) 3.92(1), 4.03(2), $^3J^*$(P–H) 8.5, 8.5 Hz; δ(CMe_3) 1.36.

(*c*) *gem*-$N_3HP_3Ph_2(OMe)_3O$ (8). The geminal bis(phenyl) derivative, $N_3P_3Ph_2Cl_4$ (5.0 g, 0.012 mol), was added to an excess of sodium methoxide and the mixture was heated under reflux for 4 h. This was diluted with diethyl ether (200 cm^3) and filtered. The solution was washed with dilute hydrochloric acid (50 cm^3), sodium hydrogencarbonate (50 cm^3), and with water (3 × 50 cm^3). The combined water washings (pH *ca.* 4) were extracted with chloroform using a continuous-extraction device. The solution was dried (Na_2SO_4) and the solvent removed. The residual oil solidified on addition of light petroleum (b.p. 40—60 °C). Recrystallisation from dichloromethane–light petroleum (1 : 4) gave 2,2,4-*trimethoxy*-4-*oxo*-6,6-*diphenylcyclotriphosphazadiene* (8), m.p. 185—187 °C (2.7 g, 58%) (Found: C, 45.0; H, 5.2; N, 10.3. $C_{15}H_{20}N_3O_4P_3$ requires C, 45.1; H, 5.0; N, 10.5%). Molecular weight in benzene by osmometry = 778 (calc. 795).

(*d*) *gem*-$N_3HP_3Cl_2(NEt_2)_3O$ (3), *gem*-$N_3HP_3Ph_2R_3O$ [R = OEt (9) *or* OPr^n (10)], *gem*-$N_3HP_3Ph_4RO$ [R = OMe (6) *or* OEt (7)], *and* $N_3HP_3R_5O$ [R = OMe (4) *or* OPh (5)]. These oxocyclotriphosphazadienes were obtained by the literature procedures described by Shaw and co-workers [6,8] and by Vîlceanu and Schulz.[7]

N.M.R. Measurements.—Hydrogen-1 n.m.r. spectra were

† The fraction of b.p. 40—60 °C was used in each experiment.

recorded on JEOL MH 100 and Bruker WH 270 spectrometers, $^{31}P-\{^1H\}$ n.m.r. spectra on a Bruker HFX-90 instrument operating at 36.43 MHz.

RESULTS AND DISCUSSION

The type of ^{31}P n.m.r. spectrum expected for the tautomeric forms of $N_3P_3R_3R'_2(OH)$ (Figure 1) is easily predicted. A summary is given in Table 1. If protonation occurs at a ring nitrogen α to the phosphoryl group the hydroxy-form: cases (*d*)—(*i*) in Table 1 are thereby excluded.

The ^{31}P n.m.r. spectra of the t-butylamino-derivatives, *gem*-$N_3HP_3(NHBu^t)_2R_3O$ [R = OMe (1) or OEt (2)], each consist of 12 lines (ABX pattern) at ambient temperature. The spectrum of the methoxy-derivative (1) is shown in Figure 2. The form of the spectrum remains unchanged at either 100 or −40 °C. This behaviour is only consistent with protonation at an α-ring nitrogen

TABLE 1

Predicted ^{31}P n.m.r. spin systems for the tautomeric forms (I)—(IV) of $N_3P_3R_3R'_2(OH)$ under different conditions of exchange

Protonation site(s)	No. of tautomers	Slow-exchange limit	Fast-exchange limit
(*a*) One α site	1	ABX *	ABX
(*b*) Two equivalent α sites	1	ABX	AX_2
(*c*) Two non-equivalent α sites	2	Two ABX	ABX
(*d*) γ Site or −OH form	1	AX_2	AX_2
(*e*) γ Site and −OH form	2	Two AX_2	AX_2
(*f*) Two equivalent α sites and γ site (or −OH form)	2	ABX and AX_2	ABX
(*g*) Two non-equivalent α sites and γ site (or −OH form)	3	Two ABX and AX_2	ABX
(*h*) Two equivalent α sites, γ site, and −OH form	3	ABX and Two AX_2	ABX
(*i*) Two non-equivalent α sites, γ site, and −OH form	4	Two ABX and Two AX_2	ABX

* The designation ABX may also include ABC or AMX spin systems in some cases.

[structures (II) and (III)], it is possible to distinguish cases (*a*), (*b*), and (*c*) in Table 1, even without a full analysis of the spectra or any knowledge of the n.m.r. parameters. If protonation occurs at the γ ring nitrogen atom or if the hydroxy-form of the compound

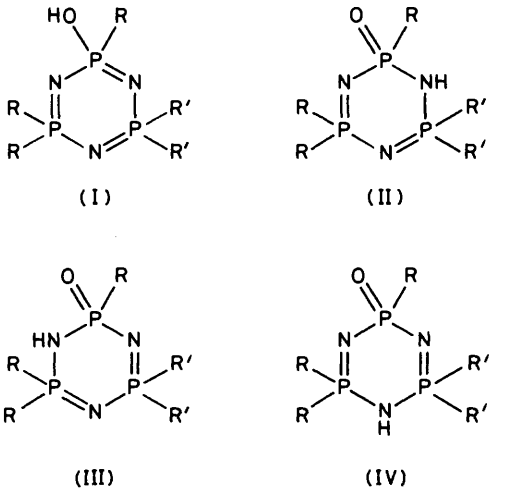


FIGURE 1 Tautomeric forms of $N_3P_3R_3R'_2(OH)$

is present [structures (IV) and (I) respectively], the spin system is indistinguishable and some knowledge of the trends in chemical shifts and coupling constants for oxocyclotriphosphazadienes and cyclotriphosphazatrienes is essential. From a consideration of their ^{31}P n.m.r. spectra, we can quickly establish that the compounds studied here do not exist either as the γ tautomer or as and with the absence of any exchange [Table 1(*a*)]. The chemical shifts (δ_P) and coupling constants [^2J(P–P)] are shown in Figures 2 and 3 and clearly indicate that compounds (1) and (2) exist as the tautomeric form (II)

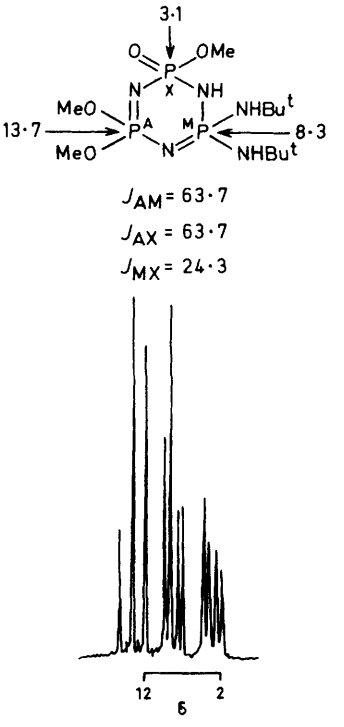
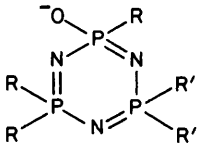


FIGURE 2 The $^{31}P-\{^1H\}$ n.m.r. spectrum of $N_3HP_3(NHBu^t)_2(OMe)_3O$ (1) in $CDCl_3$ at ambient temperature. Assignments of δ_P and ^2J(P–P) (Hz) are indicated on the structure

in solution, *i.e.* the proton resides on the ring nitrogen atom adjacent to the =PRO and $\equiv P(NHBu^t)_2$ groups.

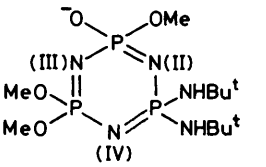
The above observation is not difficult to rationalise. It has been shown earlier [10] that substituent constants α_R and γ_R can be derived from the extensive basicity data available for cyclotriphosphazatriene derivatives. If the conjugate base of a ' hydroxy '-cyclophosphazene (shown below) is considered, the concept of substituent constants can be used to predict the preferred site(s) of protonation. It is not necessary to make assumptions regarding the value of α_{O^-} in order to calculate the relative basicities of the tautomeric forms in which protonation occurs at either ring nitrogen α to the $\equiv PR(O^-)$ group [Figure 1, structures (II) and (III)]. However, in order to predict the likelihood of the γ tautomeric form (IV) competing with either (or both) α forms, values of



α_{O^-} and γ_{O^-} must be included in the calculation. There are no direct experimental measurements for these substituent constants and their magnitude must be assumed. Values of $\alpha_{O^-} = 6.0$ and $\gamma_{O^-} = 3.0$ appear appropriate as it is anticipated that an O^- substituent should be at least comparable to an amino-substituent in its electron-releasing capability. (The latter have α_R in the range 5.6—6.0.[10]) A more detailed discussion on this point is given elsewhere.[11]

A typical basicity calculation, *viz.* for the conjugate base of $N_3HP_3(NHBu^t)_2(OMe)_3O$ (1), is shown below; the α tautomeric form (II) is favoured and the agreement with the spectroscopic findings is excellent. In the case of the diethylamino-derivative, $N_3HP_3Cl_2(NEt_2)_3O$ (3), there is an equally convincing correlation. The α tautomeric form observed in solution by ^{31}P n.m.r. spectroscopy (Figure 3) is clearly predicted by the basicity calculation (Table 2); protonation at the ring nitrogen α to $=P(NEt_2)O$ and to $\equiv P(NEt_2)_2$ is also observed in the solid state.[8]

Exchange between two equivalent α ring-nitrogen



	(II)	(III)	(IV)
α_{NHBu^t}	11.8		11.8
γ_{NHBu^t}		6.8	
α_{OMe}	3.6	10.8	7.2
γ_{OMe}	3.6		1.8
α_{O^-}	6.0	6.0	
γ_{O^-}			3.0
	25.0	23.6	23.8
$N_3P_3Cl_6$	−20.4	−20.4	−20.4
Calc. pK_a'	4.6	3.2	3.4

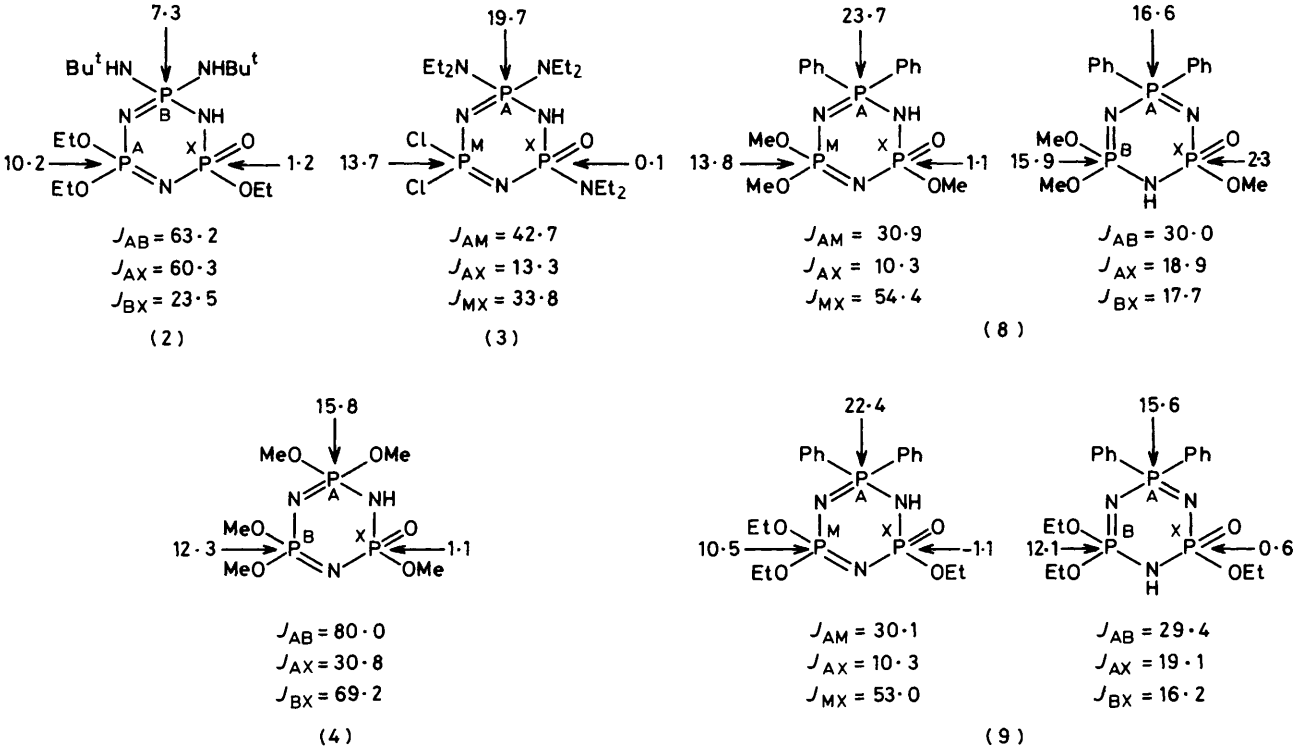


FIGURE 3 ^{31}P-{^1H} n.m.r. data (*J* in Hz) for the ' hydroxy '-cyclophosphazenes, (2) ($CDCl_3$, ambient temperature), (3) ($CDCl_3$, ambient temperature), (4) (CD_2Cl_2, −95 °C), (8) and (9) ($CDCl_3$; −50 and −40 °C respectively)

sites is exhibited by the penta-alkoxy(aryloxy)-derivative, $N_3HP_3R_5O$ [R = OMe (4) or OPh (5)]. The ^{31}P n.m.r. spectra of the phenoxy-compound (5) at ambient temperature and at −84 °C are illustrated in Figure 4. At the lower temperature, exchange is ' frozen ' and a 12-line ABX spectrum is observed as the chemical shifts of the phosphorus nuclei of the two $\equiv P(OPh)_2$ groups now differ. At ambient temperature, exchange is fast, the above nuclei become equivalent, and an AX_2 spectrum is obtained. The methoxy-analogue (4) exhibits similar behaviour in its ^{31}P n.m.r. spectrum. {Data obtained at −95 °C are shown in Figure 3; at ambient temperature $\delta[P(OMe)_2] = 14.9$, $\delta[PO(OMe)] = 2.1$, $^2J(P-P) = 48.8$ Hz.}

The derivatives, $N_3HP_3Ph_4RO$ [R = OMe (6) or OEt (7)] should also provide examples of the above exchange phenomenon [Table 1, case (*b*)]. For example, the ^{31}P n.m.r. spectrum of the methoxy-compound (6) *at ambient temperature* consists of three groups of signals: two doublets [$\delta(PPh_2)$ 24.0, $^2J(P-P) = ca.$ 4 Hz; 18.0, $^2J(P-P) = ca.$ 18.0 Hz] and two overlapping doublets, $\delta[PO(OMe)]$ −2.1, are observed. Unfortunately, the quality of this spectrum is very poor owing to the extremely low solubility of compound (6) [and also of the ethoxy-analogue (7)] in organic solvents. Nevertheless, it is interesting to note that the exchange of the proton between equivalent α sites is very slow for the tetraphenyl compound, $N_3HP_3Ph_4(OMe)O$ (6), even at ambient temperature. This slow exchange is presumably linked to the bulkiness of the four phenyl substituents.

TABLE 2

Calculated pK_a' values for the conjugate bases of the tautomeric forms (II)—(IV) of $N_3P_3R_3R'_2(OH)$

Hydroxycyclophosphazene				Calc.* pK_a' of tautomer (see Figure 1)		
	R	R'	Conjugate base	(II)	(III)	(IV)
(1)	OMe	$NHBu^t$	$N_3P_3(NHBu^t)_2(OMe)_3(O^-)$	4.6	3.2	3.4
(2)	OEt	$NHBu^t$	$N_3P_3(NHBu^t)_2(OEt)_3(O^-)$	5.1	4.1	4.1
(3)	NEt_2	Cl	$N_3P_3Cl_2(NEt_2)_3(O^-)$	−2.7	2.1	−3.3
(8)	OMe	Ph	$N_3P_3Ph_2(OMe)_3(O^-)$	1.2	1.0	0.0
(9)	OEt	Ph	$N_3P_3Ph_2(OEt)_3(O^-)$	1.7	1.9	0.7
(10)	OPr^n	Ph	$N_3P_3Ph_2(OPr^n)_3(O^-)$	2.0	2.2	1.0

* Assuming −20.4 for $N_3P_3Cl_6$ (R. A. Shaw, *Endeavour*, 1968, **27**, 74).

The derivatives, $N_3HP_3Ph_4RO$ [R = OMe (6) or OEt (7)] should also provide examples of the above exchange phenomenon [Table 1, case (*b*)]. For example, the ^{31}P n.m.r. spectrum of the methoxy-compound (6) *at ambient temperature* consists of three groups of signals: two doublets [$\delta(PPh_2)$ 24.0, $^2J(P-P) = ca.$ 4 Hz; 18.0, $^2J(P-P) = ca.$ 18.0 Hz] and two overlapping doublets, $\delta[PO(OMe)]$ −2.1, are observed. Unfortunately, the quality of this spectrum is very poor owing to the extremely low solubility of compound (6) [and also of the ethoxy-analogue (7)] in organic solvents. Nevertheless, it is interesting to note that the exchange of the proton between equivalent α sites is very slow for the tetraphenyl compound, $N_3HP_3Ph_4(OMe)O$ (6), even at ambient temperature. This slow exchange is presumably linked to the bulkiness of the four phenyl substituents.

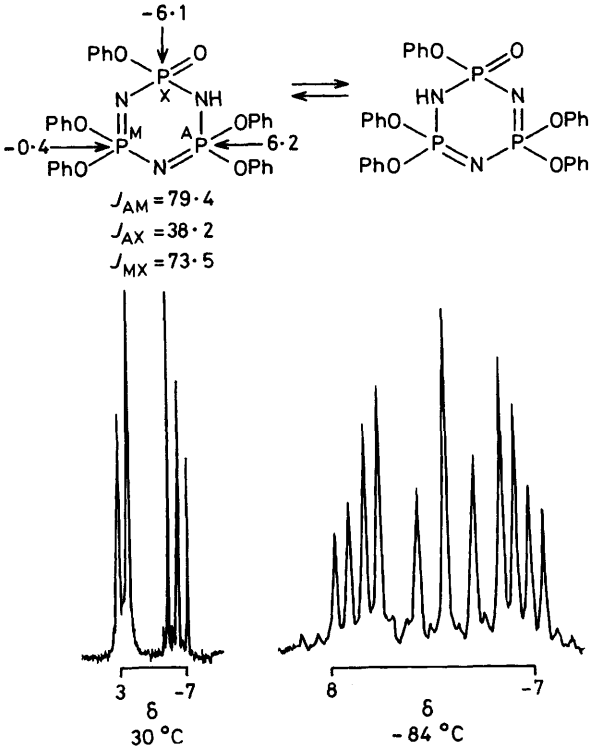


FIGURE 4 The $^{31}P-\{^1H\}$ n.m.r. spectrum of $N_3HP_3(OPh)_5O$ (5) in $CDCl_3$ (ambient temperature) and in CD_2Cl_2 (−84 °C). N.m.r. parameters (*J* in Hz) are indicated on the structural diagrams

The third kind of behaviour involving only α tautomers is that in which exchange occurs between two non-equivalent sites. The phenyl(alkoxy)-derivatives, $N_3HP_3Ph_2R_3O$ [R = OMe (8), OEt (9), or OPr^n (10)], provide examples of this tautomeric behaviour. At ambient temperature, their ^{31}P n.m.r. spectra consist only of broad, featureless absorption signals; at *ca.* −40 °C (slow exchange) two overlapping ABX spectra can be discerned, each of which arises from the presence of an α tautomeric form, and at 100 °C exchange is rapid and a single ABX spectrum is obtained. In the last spectrum, the chemical shifts of the phosphorus nuclei of $\equiv PPh_2$ and $\equiv PR_2$ (R = alkoxy) groups and the coupling constants, $^2J(P-P)$, are an approximate average of the values obtained for the individual α tautomers at low temperature.

The above points are illustrated in Figure 5, which shows the n.m.r. spectra and data for the n-propoxy-derivative (10). The ^{31}P n.m.r. data obtained at low temperature for the methoxy- (8) and ethoxy- (9) derivatives are given in Figure 3. A consideration of the δ_P values for the different α tautomeric forms of these alkoxy-derivatives, $N_3HP_3Ph_2R_3O$, (8)—(10), is informative. The values of $\delta(PPh_2)$ differ markedly for each pair of tautomers and this feature may be a result of differences in the bonding in adjacent N–P–N ring segments {more phospha*zane* character [Figure 1, structure (II; R' = Ph)] or more phospha*zene* character [structure (III)]}. In contrast, $\delta(PR_3)$(R = alkoxy) is almost identical for both tautomers, even though comparable bonding characteristics apply. Perhaps there is a conformational difference in these tautomeric forms that is influenced by the bulky $\equiv PPh_2$ group. The n.m.r. data also reveal some interesting and somewhat unpredictable differences in the values of the coupling constant

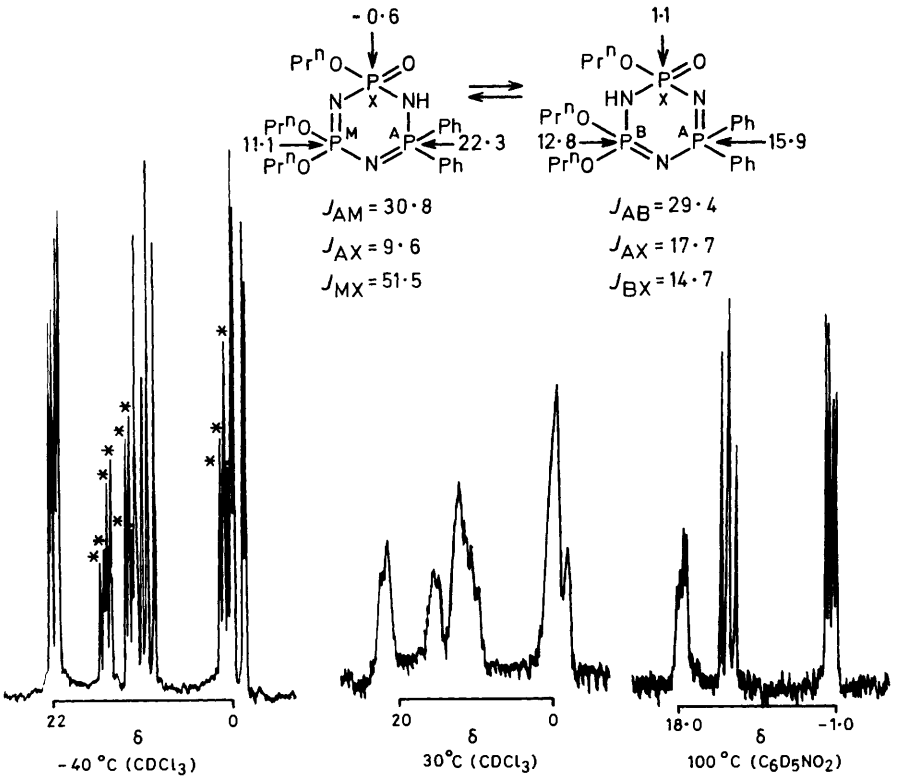


FIGURE 5 The ^{31}P-{^1H} n.m.r. spectrum of $N_3HP_3Ph_2(OPr^n)_3O$ (10) in $CDCl_3$ at ambient temperature and −40 °C [the ABX spectrum of the minor tautomer (III) is marked(*)] and in nitrobenzene (100° C). N.m.r. parameters (J in Hz) are indicated on the structural diagrams

^2J(P–P). As anticipated from our recent study [1] on six-membered, cyclic phosphorus–nitrogen compounds containing one or more phospha*zane* linkages, the coupling across the phosphazane segment [=PR_2–N(H)–P(O)=] is always lower than that across either of the formal phospha*zene* segments. The large variation in the values of ^2J(P–P) associated with phosphazene character may also depend markedly on conformational differences between each tautomeric form.

Basicity calculations for the alkoxy-derivatives (8)—(10) are given in Table 2. They correctly predict that the derivatives should exist in both α tautomeric forms and that the γ form is less favoured. It should be stressed that these calculations are approximate and that they are not intended to predict the absolute proportions of two α tautomers of similar basicity. For the alkoxy-compounds (8)—(10), ^{31}P n.m.r. spectroscopy shows that the α tautomeric form (II) (Figure 1) predominates over form (III). The ratio is *ca.* 4 : 1 for the methoxy-derivative (8) and *ca.* 2 : 1 for the n-propoxy-compound (10). This increased proportion of tautomeric form (III) observed in solution for the n-propoxy-derivative, $N_3HP_3Ph_2(OPr^n)_3O$ (10), undoubtedly reflects the greater base-strengthening effect of the n-propoxy-group compared to that of the methoxy-group.[10]

Molecular-weight measurements show that the oxocyclotriphosphazadienes reported in this study are dimeric in solution and that they presumably retain the doubly hydrogen-bonded structure found in the solid.[8,9] However, their dimeric nature does not affect the interpretation of the ^{31}P n.m.r. spectra.

Compared to the informative structural data obtained from ^{31}P n.m.r. spectra, ^1H n.m.r. spectroscopy is much less helpful for studying the tautomeric behaviour of these ' hydroxycyclophosphazenes.' In many cases, the complexity of the spectra prevents any detailed analysis. One feature of the spectra that can be utilised is the resonance arising from the proton attached to a ring nitrogen atom. This >N*H* signal occurs at low field (δ 7.3—10.0). In the 270-MHz n.m.r. spectrum of the methoxy-derivative, $N_3HP_3Ph_2(OMe)_3O$ (8), recorded at −40 °C, two sharp >N*H* signals at δ 9.8 and 9.4 (in the ratio 4 : 1) are observed, thereby confirming the ratio of the tautomers (albeit not the precise structural assignment) obtained by ^{31}P n.m.r. spectroscopy. Only four methoxy-doublets are clearly resolved at −40 °C: the ones at lower field (δ 3.37 and 3.52) arise from the =P(OMe)O group of tautomeric forms (II) and (III) respectively

Conclusions.—This study has demonstrated the following salient features. The oxocyclotriphosphazadienes investigated exist in solution as tautomers in which the hydrogen atom is bonded to a ring nitrogen atom α to the phosphoryl group. There is no evidence for γ tautomers or for the *P*-hydroxy-form. The preferred α tautomer(s) is readily established from the appearance and detailed analysis of the ^{31}P n.m.r. spectrum at different temperatures. Calculation of the relative basic character of

ring nitrogen atoms by utilising substituent constants provides a good correlation with the spectroscopic data. Thus, the combination of dynamic ^{31}P n.m.r. spectroscopy and the predictive value of basicity calculations is a powerful one and should prove useful in gaining a further insight into the complex hydrolysis reactions [3,4] of cyclophosphazene derivatives.

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